

# Peltier ac calorimeter

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## Abstract

A new ac calorimeter, utilizing the Peltier effect of a thermocouple junction as an ac power source, is described. This Peltier ac calorimeter allows to measure the absolute value of heat capacity of small solid samples with sub-milligrams of mass. The calorimeter can also be used as a dynamic one with a dynamic range of several decades at low frequencies.

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\*YHJ wishes to dedicate this paper to Dr. G. Höhne.

## I. INTRODUCTION

At the turn of the 20th century studies of heat capacity of solids at low temperatures played an important role in revealing the quantum character of Nature. [1] This example vividly illustrates the power of heat capacity measurements in physics. As a matter of fact measurements of heat capacity reveal so great a deal of information about matter that calorimetry has become an indispensable tool for modern day research in chemistry, physics, materials science, and biology. Unfortunately, however, calorimetry is a relatively insensitive method, and it is particularly difficult to obtain an accurate absolute value of heat capacity of samples with minute masses. Since new materials with interesting physical properties are usually not synthesized in quantity, it is of extreme necessity for the advance of materials science or condensed matter physics to secure a convenient means to measure absolute heat capacity of sub-milligram samples.

On another front, the generalization of calorimetry into the dynamic regime has attracted wide attention in recent years. [2] Although measurement of a thermodynamic quantity is the usual notion that is tied to calorimetry, it is possible to go beyond this traditional understanding and generalize heat capacity as a dynamic quantity. The concept of dynamic heat capacity appears natural if one recalls that static thermodynamic quantities are time-averaged (or ensemble-averaged). In other words, they are static not because they do not change in time, but because they change too rapidly on the experimental time scale. Then, suppose that a system contains a dynamic process relaxing with a characteristic time which lies within our experimental time window, this will result in a time-dependent (or frequency-dependent) heat capacity depending on the time scale of measurements. Conversely, measurements of dynamic heat capacity of condensed matter would provide insights which may not be available to other dynamic probes. Thus, the development of a convenient dynamic calorimeter for solid samples appears to be of great necessity.

In this paper, we describe a new type of the ac calorimeter, termed *Peltier ac calorimeter* (PAC), which fills both needs described above; PAC is not only a microcalorimeter capable of measuring heat capacity of sub-milligram samples but also a dynamic calorimeter with wide dynamic range. For the heat capacity measurements of a minute sample adiabatic calorimetry [3] does not appear to be suitable due to the so-called addenda problem; in other words, calorimetry requires indispensable addenda (heater and sensor) to be put on a sample

and the mass of the addenda may even be greater than that of the sample in the case of minute samples. Although one may expect the same kind of problem in ac calorimetry, [4] we have devised a way of avoiding the addenda problem in a new ac calorimeter by utilizing the Peltier effect of extremely thin thermocouple wires. It is also obvious that an ac calorimeter has a potential of being a dynamic one.

## II. PRINCIPLE OF THE PELTIER AC CALORIMETER

Suppose that a voltage difference  $\Delta V$  and/or a temperature difference  $\Delta T$  exist across a metallic wire, the electric current  $I$  and the heat current  $P$  through the wire can be expressed as [5]

$$I = -(\Delta V + S\Delta T)/R \quad (1)$$

$$P = \Pi I - K\Delta T, \quad (2)$$

where  $R$  is the resistance,  $S$  the thermoelectric power,  $\Pi$  the Peltier coefficient, and  $K$  the thermal conductance. The thermoelectric power and the Peltier coefficient are related by  $\Pi = TS$ . Now if an electric current is run through a thermocouple, consisting of two distinct metal wires, under an isothermal condition, then the junction acts as either a heat sink or a heat source depending on the current direction. The heat current  $P$  caused by this Peltier effect is directly proportional to  $I$ . If an ac electric current at an angular frequency  $\omega$ ,  $I(t) = I_0 \exp(i\omega t)$ , is applied to a thermocouple under an isothermal condition, an ac power oscillation at the same frequency will be induced at the junction by the Peltier effect. The amplitude  $P_0$  of the ac power is equal to  $P_0 = T \Delta S I_0$ ;  $P_0$  can be accurately determined, since  $\Delta S$  is well tabulated for thermocouples and the ac current can be measured with high precision. Thus it is evident that the Peltier effect of a thermocouple junction can be utilized as a power source for ac calorimetry.

Various ac calorimetric techniques with non-contact energy sources such as chopped light or light emitting diode were developed previously. [6, 7] However, it should be pointed out that these power sources can only supply heat and cannot act as a heat sink. As a consequence of this, the average temperature of a sample is always above that of the heat bath in these traditional ac calorimetric methods. (This so-called dc shift is equal to the

average dc power divided by the thermal conductance between the sample and the bath.) In addition, it is not easy in traditional ac calorimetry to determine an absolute value of heat capacity due to inaccuracy in the determination of input power and heat leak. On the other hand, the PAC which utilizes the Peltier effect as an ac power source is free from these difficulties: first, it is capable of both heating and cooling. This means that there is no dc shift in temperature, and lack of the dc shift in turn has an important implication on the working frequency range of the ac calorimeter. (See below.) Second, the power generated at a thermocouple junction can be measured with high accuracy. Third, the mass of the thermocouple junction attached to the sample is entirely negligible in most situations. All these factors make the PAC superior to previous methods in that the experimental setup is simple, it directly yields absolute values of heat capacity of sub-milligram samples, and it may be used as a dynamic calorimeter.

### III. IMPLEMENTATION OF THE PRINCIPLE

The implementation of the principle described in the previous section is rather straightforward; the schematic diagram and the photograph of the Peltier ac calorimeter we constructed is shown in Fig. 1. We made thermocouple junctions by spot-welding with chromel and constantan wires of 25  $\mu\text{m}$  (or 12  $\mu\text{m}$ ) in diameter. A couple of thermocouple junctions (TC1) were connected via copper wires to a function generator supplying an ac electric current, which was measured by a digital ammeter with 1 nA sensitivity. Using a very small amount of GE 7031 varnish for electrical insulation and good thermal contacts, one of the junctions was attached to one side of a sample (typically of linear size less than 1 mm) and the other to a copper block (heat bath). The heat bath was then attached to a closed-cycle He refrigerator and its temperature was controlled within  $\pm 2$  mK stability in the range of 15–420 K. A digital voltmeter was used to read the voltage difference across another thermocouple junction (TC2) attached to the other side of the sample. From the voltage readings, we could measure the sample temperature with the sensitivity of 1.67 mK at 15 K and 0.14 mK at 420 K.

Since the mass of the thermocouple junctions and the varnish is completely negligible compared to the sample mass even for sub-milligram samples, the amplitude of the temper-

ature oscillation  $\delta T_\omega$  at the imposed frequency (measured by TC2) can be written as [6]

$$\delta T_\omega = \frac{P_0}{\omega C_p} \left( 1 + \frac{1}{\omega^2 \tau_{ext}^2} + \omega^2 \tau_{int}^2 + \frac{2K_b}{3K_s} \right)^{-1/2}, \quad (3)$$

where  $C_p$  is the sample heat capacity,  $\tau_{ext}$  the external or sample-to-bath relaxation time,  $\tau_{int}$  the internal diffusion time in the sample,  $K_b$  the thermal conductance of the link between the sample and the bath, and  $K_s$  the thermal conductance of the sample. Since only the thin thermocouple wires of diameter 12 or 25  $\mu\text{m}$  provide paths for heat conduction from the sample to the heat bath,  $K_b$  is extremely small and negligible compared to  $K_s$ . And the third term in the parenthesis of Eq. (3) can be neglected. Thus, if one can select the frequency range of  $1/\tau_{ext} \ll \omega \ll 1/\tau_{int}$ , heat capacity may be directly obtained from  $C_p = P_0/\omega\delta T_\omega$ .

In addition to providing a means for measuring the absolute value of heat capacity of minute solid samples, the PAC possesses a distinct ability to function as a dynamic calorimeter. This capability of the PAC stems from the fact that  $K_b$  is extremely small as noted above (Heat conduction paths are provided by microns thick thermocouple wires only.) and thus  $\tau_{ext}$  is exceedingly large. Large  $\tau_{ext}$  then allows a wide frequency range where the relationship  $C_p = P_0/\omega\delta T_\omega$  holds. This situation is contrasted to that of traditional ac calorimeters where one is required to have a reasonable size of  $K_b$ , because otherwise the dc shift of the sample due to a dc power would become prohibitively large. (Remember that the dc shift is given by the dc power divided by  $K_b$ .) This size requirement of  $K_b$  then places a limit to the working frequency range of the ac calorimeter by decreasing  $\tau_{ext}$ . Note that the origin of this limitation of the traditional ac calorimeter goes to the fact that the energy source is only capable of heating, but not cooling. On the other hand, the energy source of the PAC is able to both heat and cool, the average temperature of the sample is the same as the bath temperature, and the PAC can afford to have exceedingly small  $K_b$  and long  $\tau_{ext}$ .

#### IV. PERFORMANCE OF THE PELTIER AC CALORIMETER

The performance of the PAC was tested with small pieces of synthetic sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ), the standard material designated by NIST. [8] We first examined the induced temperature oscillation in TC2, in response to an oscillating electric current in TC1, at 30 K, 150 K, and 320 K with a test sample of mass 0.54 mg and dimension  $1 \times 0.5 \times 0.3 \text{ mm}^3$ . The frequency and amplitude of the electric current were 0.25 Hz and 0.4 mA, respectively. From Fig. 2(a)

and (b), it is seen that nice temperature oscillations at the applied frequency are obtained at 150 K and 320 K. However, Fig. 2(c) reveals that a significant amount of the second harmonic appears at 30 K. It is readily clear that this second harmonic originates from Joule heating in the thermocouple wires. To precisely determine  $\delta T_\omega$  which will yield heat capacity, the raw data were fitted to a sinusoidal function containing the fundamental and second harmonic terms. Fig. 2(d) shows the power amplitude at the fundamental and second harmonics as a function of temperature. The power amplitude at the fundamental were converted from the measured  $I_0$  using the table for  $\Delta S$ . [9] The Joule heating part was obtained from the fitting procedure. Above 50 K, the Joule heating effect is completely negligible; however, there appears an increasing amount of the second harmonic as temperature decreases below 50 K. This is probably caused by the reduction in thermal resistance of the thermocouple wires at low temperatures, and thus part of the heat generated along the wires flows back toward the sample. However, the existence of the second harmonic does not cause too much problem in the heat capacity measurements, since the governing equation for the present problem is linear and therefore one needs only to measure the signal at the fundamental frequency. Nevertheless, it is desirable to reduce the Joule heating as much as possible to attain the sensitivity.

The dynamic characteristics of the PAC was then checked by measuring the frequency dependence of  $\delta T_\omega$  for the test sample (0.54 mg) at a fixed amplitude of the applied current. Fig. 3 is the plot of the results obtained at three temperatures. It is seen from the figure that  $\delta T_\omega$  is proportional to  $f^{-1}$  in the whole measured frequency range at high temperatures (150 K and 320 K), and the figure clearly illustrates that the PAC is indeed a dynamic calorimeter. The data obtained at 30 K, however, shows a large deviation from the  $f^{-1}$  behavior at frequencies below 0.13 Hz. This is caused by the fact that the smallness of  $K_b$  is compensated by a rapid decrease in heat capacity at low temperatures, and the external relaxation time  $\tau_{ext}$  becomes short enough to be comparable to the oscillation period at 0.13 Hz. This compensation effect is unavoidable and the dynamic capability of the PAC is of limited use below roughly liquid nitrogen temperature. It may be also noted that the deviation from the  $f^{-1}$  behavior is also expected at high frequencies, since our power source is an extremely local one and the internal diffusion time will interfere above a certain frequency. This high cutoff should be size-dependent, and present no problem for small samples.

In order to ascertain the capability of the PAC as a microcalorimeter, we carried out the heat capacity measurements for two test samples of  $\alpha\text{-Al}_2\text{O}_3$  with mass 0.54 mg and 2.25 mg. The measuring frequency was set at 0.25 Hz and the measured temperature range was from 15 K to 420 K. It is stressed that background subtraction, required in most calorimetric methods, is not necessary for the PAC. Fig. 4 (a) is the plot of the heat capacity data for two sapphire samples. The two sets of data coincide very well and display excellent reproducibility of the PAC. Also plotted in the figure is the reference data ( $C_p^{ref}$ ) of the same material. [8] The agreement is again excellent in the whole temperature range from 15 K to 420 K. In order to estimate the accuracy and precision of the PAC, we plotted the residual heat capacity values, *i.e.*, ( $C_p - C_p^{ref}$ ) in Fig. 4(b). From the figure, we estimate the absolute accuracy for heat capacity of a sub-milligram sample to be  $\pm 3\%$  for the temperature range of 30–150 K and  $\pm 1\%$  for 150–420K. At temperatures below 30 K, the absolute accuracy worsens due to very small values of heat capacity of  $\alpha\text{-Al}_2\text{O}_3$  and becomes even more than 10%. However, the precision is better than 0.5% in the whole temperature range of 15–420 K.

## V. FUTURE OUTLOOK

Having demonstrated the capability of the PAC as a microcalorimeter and dynamic calorimeter, we briefly outline the possible extensions of the PAC, which are currently under development. First of all, it should be noted that the PAC would function as a microcalorimeter even at Helium temperatures if cryogenic thermocouple wires of Au-Fe or Cu-Fe are used. This replacement of thermocouples would have an additional effect of suppressing unwanted Joule heating. A more novel extension of the PAC would be the Peltier thermal microscope, which would enable to measure local thermophysical properties of matter at submicron length scales. Here it is proposed that the tip for a atomic force microscope is replaced by a thermocouple tip. An important feature of our proposal is that the thermocouple tip here is not just a temperature sensor, but it plays dual roles of a heater and sensor. For this purpose, we have shown that a single junction can indeed be used as both a heat source and sensor simultaneously. [10] The successful development of the Peltier thermal microscope would be an exciting and important event for this so-called nano-age when the submicron local thermophysical properties are in great demand.

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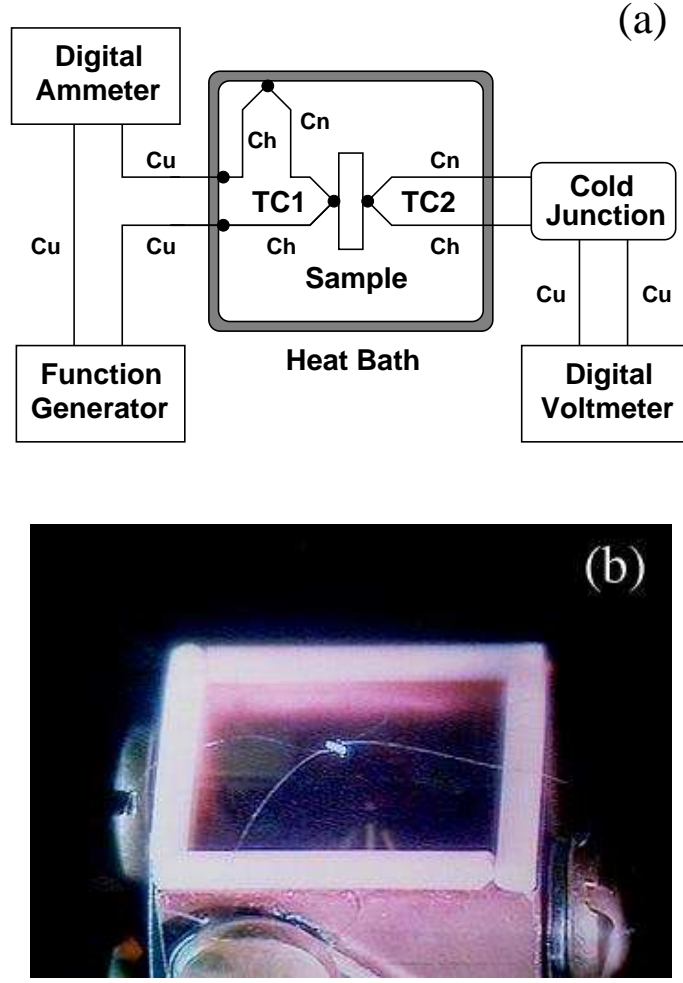


FIG. 1: (a) The schematic diagram of the Peltier ac calorimeter. Ch, Cn, and Cu denote chromel, constantan, and copper wires, respectively. Wires of either diameter  $25\ \mu\text{m}$  or  $12\ \mu\text{m}$  are used. A copper block plays a role of heat bath. A function generator applies an oscillating current to Ch-Cn thermocouples (TC1) in contact with the sample, and a digital voltmeter measures an ensuing voltage oscillation from another thermocouple (TC2) attached to the sample. (b) The photograph of the Peltier ac calorimeter. The linear dimension of the sample is approximately 1 mm, and the diameter of the thermocouple wires is  $25\ \mu\text{m}$ .

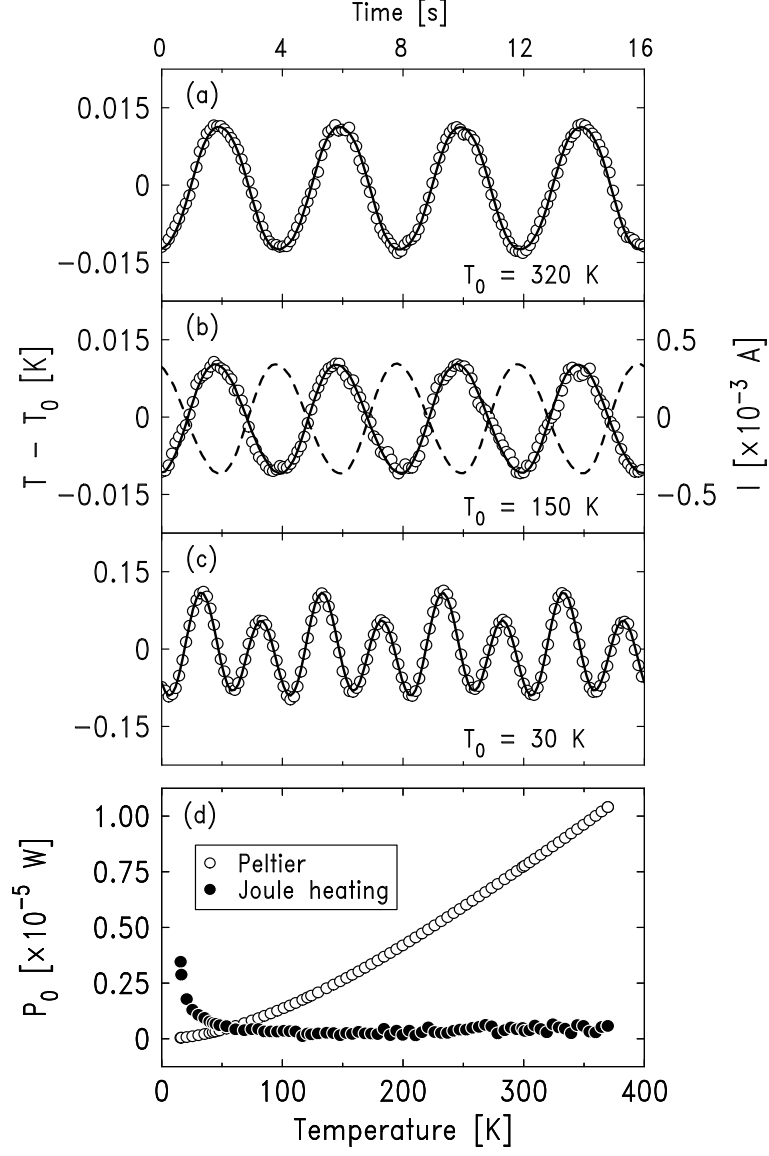


FIG. 2: The data of the sample temperature oscillation measured at 30 K (a), 150 K (b), and 320 K (c). The test sample was a piece of sapphire with mass 0.54 mg and dimension  $1 \times 0.5 \times 0.3$  mm<sup>3</sup>. The broken line of (b) shows the electric current oscillation. The solid lines indicate the fitting results with the fundamental and second harmonics, and  $T_0$  represents the dc component. (d) The amplitude of the power oscillations at the fundamental (Peltier) and second harmonics (Joule).

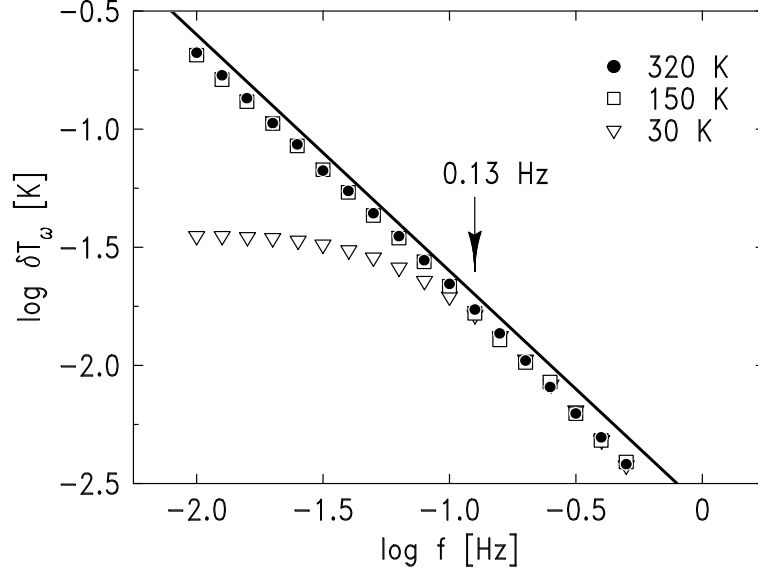


FIG. 3: The dynamic characteristics of the Peltier ac calorimeter. The magnitude of temperature oscillation  $\delta T_\omega$  is plotted as a function of frequency. The thick solid line represents the  $f^{-1}$  behavior. Note that the  $f^{-1}$  law is well obeyed in the whole frequency range at high temperatures; the PAC is able to function as a dynamic calorimeter. The arrow indicates the low cutoff frequency below which the deviation from the  $f^{-1}$  behavior appears at low temperatures.

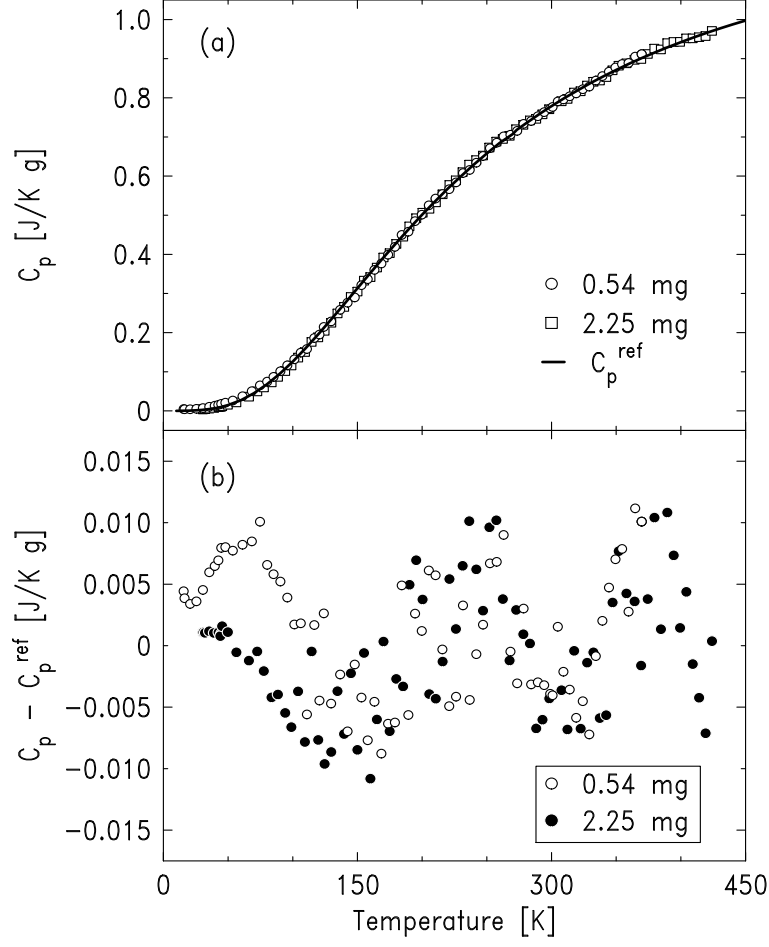


FIG. 4: (a) Specific heat capacity of the standard synthetic sapphire.  $C_p$  of two samples with mass 0.54 mg and 2.25 mg is plotted. The solid line represents reference values from Ref. [8]. (b) The residual values,  $(C_p - C_p^{ref})$ , are plotted.